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⑭ポリパラベン酸組成物

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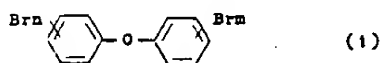
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明 細 書

1 発明の名称 ポリパラベン酸組成物

2 特許請求の範囲

ポリパラベン酸と一般式(1)

(但し、式中 $x + y = 6 \sim 10$)

で表わされる化合物とからなるポリパラベン酸
組成物。

3 発明の詳細な説明

本発明はポリパラベン酸組成物に関するものであり、さらに詳しくは、ポリパラベン酸(以下、PPAという。)本来の諸特性及び外観をなんら損うことなく優れた難燃性を示すPPA組成物に関するものである。

PPAは、機械的特性、電気的特性、化学的特性、耐熱性及び寸法安定性等の諸特性が他のプラスチックよりも優れていることから、プラスチックフィルムを基体としたフレキシブル印刷

回路配線板、IO用フィルム、電気絶縁用フィルム及び成型品としての電気、機械部品等への用途が期待されている。

一方、これらの工業用材料には、機械的特性、化学的特性の他に、火災に対する安全性、すなわち、難燃性が強く要求されており、現状では難燃性の有無にかんが、工業用材料としての用途を拡大する可能性を左右するといつても過言ではない。

しかるに、PPAは前記の優れた諸特性を有している反面、難燃性が充分とは言えず、難燃性を付与することが強く望まれている。

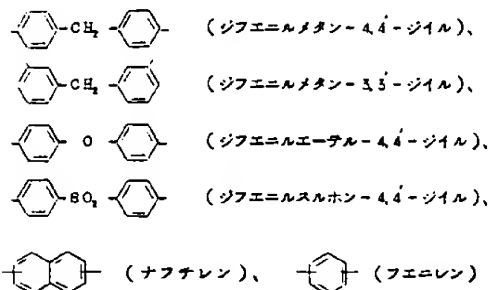
本発明の目的は、PPA本来の優れた機械的特性、電気的特性、化学的特性及び外観をなんら損うことなく、難燃性を改良することにある。

一般に有機重合体に難燃性を付与する方法としては、無機化合物を多量に添加する方法、有機ハロゲン化合物を添加する方法、リン化合物を添加する方法、又はこれらを併用する方法等があるが、難燃性の付与のみを目的として、こ

$$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array} \right] \quad (2)$$

(但し、 ΔF はアリーレン残基を示す。)

を基本単位とする単独重合体または共重合体であるが上記一般式における ΔF (アリーレン残基)としては、



等である。そしてその意合体あるいは共成合体の固有粘度（DMF 25℃で）が0.4～2.5のもの

本発明に用い得る PPA は、米国特許第 3542897 号明細書、同 3591562 号明細書、特公昭 47-19715 号公報あるいは ACS Polymer Preprints 12 (No. 1) P162 (1971) 等に開示されている一般式(2)、

$$\begin{array}{ccc}
 \begin{array}{c} \text{O} \\ \parallel \\ -\text{R}-\text{N}-\text{C}-\text{N}-\text{R}- \\ | \quad | \\ \text{N} \equiv \text{C} - \text{C} = \text{O} \end{array} & \xrightarrow{\text{H}_2\text{O}} & \begin{array}{c} \text{O} \\ \parallel \\ -\text{R}-\text{N}-\text{C}-\text{N}-\text{R}- \\ | \quad | \\ \text{H N} = \text{C} - \text{C} = \text{O} \end{array} \\
 \\
 \begin{array}{c} \text{O} \\ \parallel \\ -\text{R}-\text{N}-\text{C}-\text{N}-\text{R}- \\ | \quad | \\ \text{N} = \text{C} - \text{C} = \text{O} \end{array} & \xrightarrow{\text{H}_2\text{O}} & \begin{array}{c} \text{O} \\ \parallel \\ -\text{R}-\text{N}-\text{C}-\text{N}-\text{R}- \\ | \quad | \\ \text{C} = \text{C} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array} + \text{NH}_3
 \end{array}$$
$$\begin{array}{ccc}
 -R-NCO + HCN & \xrightarrow{\text{触媒}} & \begin{array}{c} H \quad O \\ | \quad || \\ -R-N-C-CN \end{array} \\
 \\
 \begin{array}{c} H \quad O \\ | \quad || \\ -R-N-C-CN \end{array} + -R-NCO & \xrightarrow{\text{触媒}} & \begin{array}{c} O \\ || \\ -R-N-C-N-R- \\ | \quad | \\ N \equiv C-C=O \end{array}
 \end{array}$$

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シクロヘキサノン、1,3-ジオキソラン等、の存在下で混合する方法等が簡便で好ましい。又、PPAの製造段階に臭素化合物を添加する方法でもよい。すなわち、前記の米国特許第3542897号明細書、或いは同第3591562号明細書に記載されている製造方法において、重合溶媒中に添加混合することもできる。この場合は、重合開始段階或いは重合途中段階よりも重合終了段階、特にPPAをPPAの非溶解性の溶媒中に沈析出させる前の段階で添加混合するのが好ましい。又この際、本発明の組成物を沈析出させる溶媒、さらに洗浄する溶媒は、臭素化合物を溶解させないものを選択する必要がある。

PPAと臭素化合物の混合割合は、PPA 100重量部に対して臭素化合物1~20重量部、望ましくは3~10重量部である。これより少ない割合には、充分耐熱性が発現できないし、又これより多い割合には、PPA本来の優れた特性を損つてしまう場合があり好ましくない。

・耐熱性 目社法

(PPA試片を200℃に設定したギヤーオープン中に吊し、一定時間経過後に取り出し、折り曲げテストを行なう。この折り曲げテストに合格するオープンライフを耐熱性の尺度とする。)

・制 断 強 度 JIS C-6481(180°熱)

・半 田 耐 熱 性 JIS C-6481

ここで耐熱指数は一定量の試料が空气中に於て断断を懸架する場合に必要とする空気量の相対値を示すもので、断断が大きい程、自己消火性内至燃焼性であることを示す。

耐熱指数とUL規格に依る耐熱性の表示には次の関係がある。

耐熱指数	UL規格
22.5>	94UD
22.5~28	94V1 or 94V2
28<	94V0

実施例1

米国特許第3542897号明細書の記載に基づいて上記PPAの一般式におけるArとしてジフェニルメタン-4,4'-ジイル基を有する芳香

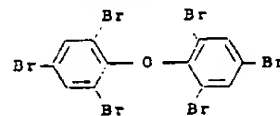
本発明は上記の構成を採ることにより、本発明のポリペラベン酸組成物は、PPA本来の優れた機械的特性、電気的特性、化学的特性及び外観をなんら損うことなく、高性能の難燃性を有しており、圧縮成形法、流延式フィルム成形法、溶液粉末法等の成形法で成形した、モールドイング、フィルム、ファイバー等は優れた性能を発揮するものである。

以下に本発明を実施例にて詳細に説明するが本発明はその発明を越えない限り、これらになんら限定されるものではない。なお、実施例記載の部は、全て重量部を要す。

なお実施例における測定試験方法は次の通りである。

- ・引張強度、引張伸び ASTM D-882
- ・弾索指数(L.O.I.) JIS K-7201
- ・自己消火性 UL規格UL-94
- ・体積抵抗値 ASTM D-257
- ・絶縁破壊電圧 ASTM D-149
- ・耐電圧、誘電正接 ASTM D-150

極成、71^{DMP}₁₀₀²⁵⁰ = 110のPPAを合成した。得られたPPAは粗い粉末状態であつた。この合成したPPAの粉末16部に下式で示される臭素化合物をそれぞれ、0.5部、1.0部、1.5部添加したものを100部のDMFに溶解し攪拌混合することにより3種類の均一混合溶液を調製した。



これらの3種類の混合溶液を真空脱泡後、ガラス板上に塗布して150℃で10分間乾燥して、その後ガラス板上からそこで得たフィルムを剥離し、次に280℃で10分間乾燥し厚さ50μの3種類のPPA組成物のフィルムを得た(比較1, 2, 3)。また比較例として上記臭素化合物を添加しない他は、全て同様の方法にて厚さ50μのPPAフィルムを得た(比較例1)。得られたこれらのPPA組成物のフィルム及びPPAフィルムの機械的強度、機械的強度の試験

性、難燃性、電気的特性を表-1に示すが本発明のPPA組成物は、PPA本来の諸特性を何ら損うことなく優れた難燃性を有している。

実施例2

実施例1で得られたPPA粉末100部に対して、下式で示される臭素化合物60部を添加し、ヘンシェルミキサーにてドライブレンドした後、得られたPPA組成物のパウダーを、350℃に温度設定した圧縮成形機を用いて厚さ50μのフィルムとした。得られたフィルムの諸物性を表-1に示すが本発明のPPA組成物はPPA本来の諸特性を何ら損うことなく優れた難燃性を有している(実験4)。

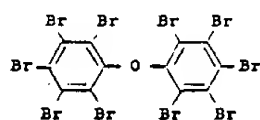


表 - 1

評価項目	単位	比較例-1	実験-1	実験-2	実験-3	実験-4
1) 臭素化合物添加量 (PPA100部に対する部)	部	0	31	63	94	60
2) フィルム厚み	μ	50	50	50	50	50
3) フィルム色相、透明性		良	良	良	良	良
4) 引張強度(破断点)	Kg/cm ²	1200	1250	1200	1130	1210
5) 引張伸び(破断点)	%	16	15	16	15	16
6) 耐熱性(200℃) (折り曲げテスト)	時間	300	350	350	310	350
7) 酸染指数(L.O.I.)	%	215	225	315	330	300
8) 自己消火性(UL-94)	Classification	94 HB	94 V-0	94 V-0	94 V-0	94 V-0
9) 体積抵抗	Ω-cm	3.9×10 ⁸	3.7×10 ⁸	3.6×10 ⁸	3.5×10 ⁸	3.7×10 ⁸
10) 絶縁破壊電圧	V/mil	4000	3950	4100	4000	4100
11) 誘電率(50Hz)		4.0	4.0	4.1	4.0	4.1
12) 体積正接		0.003	0.003	0.003	0.003	0.003

実施例 3

米国特許第3542897号明細書の記載に基づいて前記PFAの一般式におけるArとしてジフェニルエーテル-4,4'-ジイル基を有する固形粘度 $\frac{DMF}{250^\circ C} = 0.95$ のPFAを合成した。得られたPFAの粉末16部に、実施例1で用いた臭素化合物をそれぞれ0.5部、1.0部、1.5部添加したものを100部のNMPに溶解し攪拌混合することにより3種類の均一混合溶液を調製した。これら3種類の混合溶液を実施例1と全く同様の方法により厚さ50 μ の3種類のPFA組成物のフィルムを得た(実験5, 6, 7)。また比較例として上記臭素化合物を添加しない他は、全て同様の方法にて厚さ50 μ のPFAフィルムを得た(比較例2)。これらのPFA組成物のフィルム及びPFAフィルムの諸特性を表-2に示すが本発明のPFA組成物はPFA本来の優れた諸特性を何ら損うことなく優れた燃焼性を有している。

実施例 4

実施例3で得られたPFAの粉末100部に対して、下式で示される臭素化合物の粉末6部を添加し、ヘンシェルミキサーにてドライブレンドした後、350 $^\circ C$ に温度設定した圧縮成形機を用いて厚さ50 μ のフィルムとした。得られたフィルムの諸特性を表-2に示すが本発明のPFA組成物は優れた燃焼性を有している(実験8)。

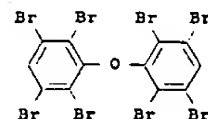


表 - 2

評価項目	単 位	比較例-2	実験-5	実験-6	実験-7	実験-8
1) 臭素化合物添加量 (PFA100部に対する部)	部	0	3.1	6.5	9.4	6.0
2) フィルム厚み	μ	50	50	50	50	50
3) フィルム色相・透明性		良	良	良	良	良
4) 引張強度(破断点)	Kg/cm ²	1500	1500	1280	1280	1290
5) 引張伸び(破断点)	%	20	20	19	18	19
6) 耐熱性(200 $^\circ C$) (折力強けテスト)	時間	350	360	340	350	350
7) 酸素指数(L.O.I.)	%	21.0	30.0	31.5	33.5	32.0
8) 自己消火性(UL-94)	Classification	94HB	94V-0	94V-0	94V-0	94V-0
9) 体 積 抵 抗	$\Omega \cdot cm$	5×10^6	4.9×10^6	5.0×10^6	4.7×10^6	4.9×10^6
10) 絶 縁 破 壊 電 圧	V/mil	3800	3800	3800	3800	3800
11) 漏 電 率(50HZ)		3.7	3.9	3.8	3.7	3.9
12) 誘 電 正 接		0.005	0.005	0.005	0.005	0.005

実施例 5

米国特許第3,542,897号明細書の記載に基づいたPPA合成段階におけるPPA組成物の製造方法についての実施例を示す。即ち、184ccのNMP中に53gのシアニ化水素を溶解させた溶液と、1000ccのNMPに490gの4,4'-ジフェニルメタンジイソシアネートを溶解させた溶液を25ccの飽和シアニ化ナトリウム溶液を含む6000ccのNMP溶液中に同時に滴下し重合反応を行なつた。シアニ化水素溶液、4,4'-ジフェニルメタンジイソシアネート溶液を約7分間で滴下し終つた後、30分間撹拌し続けた。その後その重合反応溶液中に20gのトリエチルアミンを添加し更に30分間撹拌し続けた。こうして得られた重合反応溶液中に325gの実施例1で用いた臭素化合物を添加混合し均一溶液とした。この均一溶液を大量のメタノール中に注ぎ、十分撹拌しながら粉末状生成物を析出た後、更にメタノールで洗浄し乾燥させることにより570gの本発明のPPA

組成物のパウダー（固有粘度 $\eta_{inh}^{DMF} = 1.10$ ）を得た。このPPA組成物のパウダー17部を100部のDMFに溶解させ撹拌混合することによりPPA組成物の溶液を調製した。この溶液を用いて、実施例1と全く同様の流延法により50 μ のフィルムを得た（実験9）。また比較例として実施例1で用いた臭素化合物を添加しない他は、全て同様の方法にて厚さ50 μ のPPAフィルムを得た（比較例3）。これらの得られたフィルムの諸特性を表-3に示すが本発明のPPA組成物は優れた機械性を有している。

2/5 (12)

表 - 3

評価項目	単 位	比較例 - 3	実 験 - 9
1) 臭素化合物添加量 (PPA100部に対する部)	部	0	6
2) フ ィ ル ム 厚 み	μ	50	50
3) フ ィ ル ム 色 相、透明性		良	良
4) 引張強度（破断点）	Kg/cm ²	1250	1290
5) 引張伸び（破断点）	%	16	17
6) 耐熱性（200℃） (折り曲げテスト)	時間	310	340
7) 酸素指数（L.O.I.）	%	21.5	22.5
8) 自己消火性（UL-94）	Classification	94 HB	94 V-0
9) 体 積 抵 抗	$\Omega \cdot \text{cm}$	3.9×10^{16}	3.8×10^{16}
10) 絶縁破壊電圧	V/mil	4100	4000
11) 誘電率（50Hz）		4.0	3.9
12) 誘電正接		0.004	0.004

実施例 6

NMP に実施例 1 で得られた PPA の粉末を 1 重量% 溶解した溶液をプリント回路用に処理された 3.5 μ の厚さの銅箔〔福田金属製商品名 CP3T5〕に塗布し、その上に実施例 1 の実施 2 で得られた PPA 組成物のフィルムを重ねて 180℃ で 2 分間、10 kg/cm² の圧力で熱プレスを行ない、200℃ ~ 220℃ で 30 分間、270℃ ~ 290℃ で 20 分間乾燥を行なった。その結果得られた複合体 (PPA 銅箔板) は、270℃ の半田浴上に 1 分間以上耐え、剥離強度は 17 kg/cm² であつた。このフィルムの溶媒残存率は 0.1 重量% 以下であり、また長時間の室内保存でも上記物性の経時変化は認められなかつた。以上の様に本発明で得られる PPA 組成物のフィルムはフレキシブル印刷回路配線板に十分適用可能である。

実施例 7

NMP に実施例 5 で得られた PPA の粉末を 1 重量% 溶解した溶液をプリント回路用に処理され

た 3.5 μ の厚さの銅箔〔福田金属製商品名 CP3T5〕に塗布し、その上に実施例 3 の実施 6 で得られた PPA 組成物のフィルムを重ねて 180℃ で 2 分間、10 kg/cm² の圧力で熱プレスを行ない、200℃ ~ 220℃ で 30 分間、270℃ ~ 290℃ で 20 分間乾燥を行なった。その結果得られた複合体 (PPA 銅箔板) は、270℃ の半田浴上に 1 分間以上耐え、剥離強度は 17 kg/cm² であつた。このフィルムの溶媒残存率は 0.1 重量% 以下であり、また長時間の室内保存でも上記物性の経時変化は認められなかつた。以上の様に本発明で得られる PPA 組成物のフィルムはフレキシブル印刷回路配線板に十分適用可能である。

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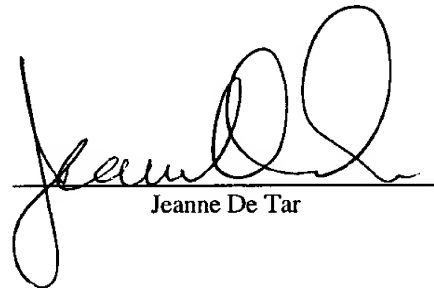
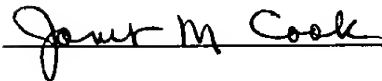
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TRANSLATION FROM JAPANESE INTO ENGLISH

I, Jeanne De Tar, Manager of THE LANGUAGE SERVICE, Inc., translation bureau at 806 Main Street, Poughkeepsie, New York, hereby certify that the attached translation of the Unexamined Patent Publication [Kokai] No. 53-45,353 dated April 24, 1978, was prepared by Frederic Metreud from the original document submitted to him in the Japanese language.

I further certify that I know Frederic Metreud to be a professional translator thoroughly familiar with the Japanese and English languages and that the attached translation is a true, complete, and correct English version of the original document to the best of my knowledge and belief.


Jeanne De Tar

Sworn to before me on this
5th day of June, 1997
Poughkeepsie, New York

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(54) Title of the Invention: POLYPARABANIC ACID COMPOSITIONS

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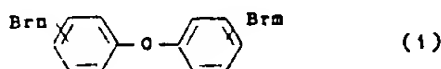
SPECIFICATION

1. Title of the Invention

Polyparabanic Acid Compositions

2. Claim

A polyparabanic acid composition comprising polyparabanic acid and a compound represented by general formula (1)



(where $n+m$ is from 6 to 10).

3. Detailed Description of the Invention

The present invention relates to polyparabanic acid compositions. More specifically, it relates to polyparabanic acid (hereinafter abbreviated as PPA) compositions having excellent fire retardance, in which the properties and appearance intrinsic to PPAs are not compromised whatsoever.

Because the various properties of PPAs, including their mechanical properties, electrical properties, chemical properties, heat resistance and dimensional stability, are better than those of other plastics, these show promise for use in flexible printed circuit boards having a plastic film substrate, films for integrated circuits (IC), films for electrical insulation, and molded electrical and mechanical components.

At the same time, in addition to mechanical properties and chemical properties, it is strongly desired that, for industrial materials applications, PPAs also have safety with respect to fires, and specifically fire retardance. It would be no exaggeration to state that the presence or absence of fire retardance currently has a strong influence on the potential for expansion in the use of this as an industrial material.

Although PPAs have the various outstanding properties mentioned above, because they have an inadequate fire retardance, there is a strong desire that they be conferred with fire retardance.

The object of the present invention is improve the fire retardance of PPAs without compromising in any way the excellent mechanical properties, electrical properties, chemical properties or appearance inherent to these materials.

The methods generally used for conferring organic polymers with fire retardance include methods involving the addition of a large amount of inorganic compounds, methods involving

the addition of organic halogen compounds, methods involving the addition of phosphorus compounds, and methods that use combinations of these. However when the amount in which these fire retardance-imparting agents are added is increased solely for the purpose of conferring fire retardance, the various properties inherent to the organic polymer are generally diminished. Hence, the emphasis has in fact been placed on finding distinctive combinations of organic polymers and these fire retardance-imparting agents, or methods for imparting [fire retardance].

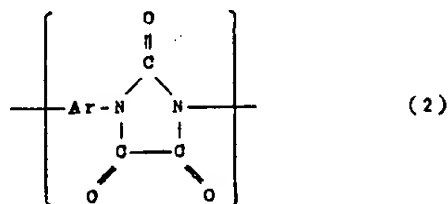
In light of the above, the inventors conducted intensive research on imparting fire retardance to PPAs, as a result of which they ultimately arrived at the present invention.

That is, the gist of the present invention is a polyparabanic acid composition comprising polyparabanic acid and a compound represented by general formula (1)

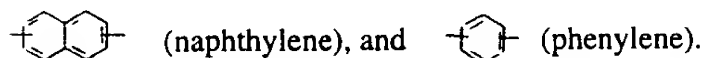
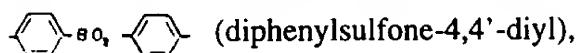
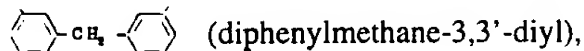
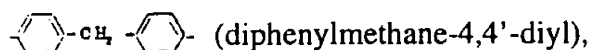


(where n+m is from 6 to 10).

The PPAs that may be used in the present invention are homopolymers or copolymers in which the basic units have general formula (2)

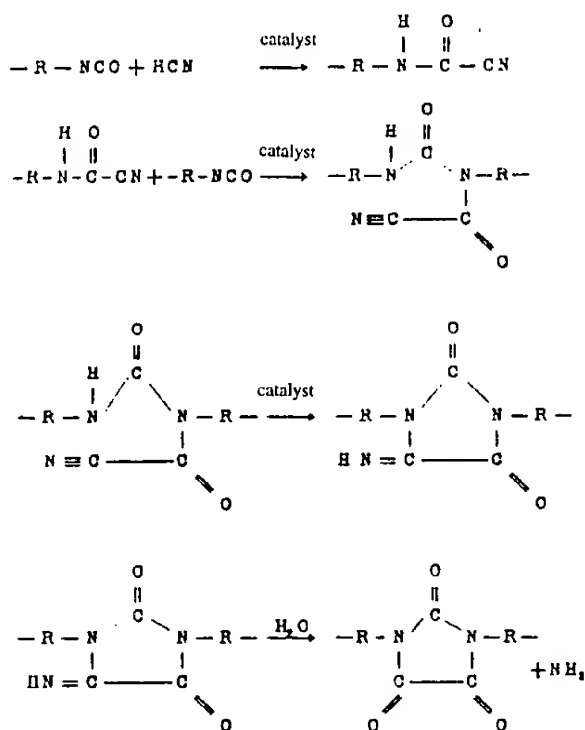


(where Ar is an arylene residue), such as those disclosed in, for example, U.S. Patent Nos. 3,547,897 and 3,591,562, Japanese Examined Patent Publication [Kokoku] No. 47-19,715 (1972), and *ACS Polymer Preprints* **12**, No. 1, p. 162 (1971). Examples of the Ar (arylene residue) in the above general formula include



The intrinsic viscosities (DMF, 25°C) of these polymers or copolymers are preferably from 0.4 to 2.5, with viscosities of from 0.6 to 1.2 being especially desirable for obtaining composites having a high degree of flexibility.

To give a brief description of the method for synthesizing PPAs, this consists of polymerizing hydrogen cyanide and a diisocyanate compound in a basic solvent (e.g., N-methylpyrrolidone, dimethylformamide, dimethylsulfoxide) and in the presence of a suitable catalyst. The polymerization catalysts used in USP 3,547,897, for example, were alkali metal cyanides, and that used in USP 3,591,562 was pyridine.



The PPA compositions of the present invention can be prepared from PPA and a compound having general formula (1) (hereinafter referred to as "bromine compound"). Methods for doing this that are preferable on account of their simplicity include a method whereby the PPA and the bromine compound are simply mixed, a method whereby the PPA and the bromine compound are kneaded while being heated and melted, and a method whereby the PPA and the bromine compound are mixed in the presence of a solvent such as dimethylformamide (DMF), N-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO), dimethylacetamide, cresols, cyclohexanone and 1,3-dioxolane. A method in which the bromine compound is added at the PPA preparation stage is also possible. That is, in the production methods cited in the specifications of above-mentioned USP 3,547,897 or 3,591,562, addition and mixing into a polymerization solvent can also be carried out. In this case, it is preferable to carry out addition and mixing at the completion of polymerization rather than at the start or during the course of polymerization, and especially at the stage prior to inducing the precipitation and settling of PPA in a solvent that does not dissolve PPA. In addition, it is necessary to select at this time solvents

which do not dissolve the bromine compound for use as the solvent for inducing precipitation and settling of the composition of this invention and as the washing solvent.

The mixing ratio of PPA and the bromine compound is 1-20 parts by weight, and preferably 3-10 parts by weight, of the bromine compound per 100 parts by weight of the PPA. When the ratio is lower than this, sufficient fire retardance cannot be exhibited, and when it is higher than this, the excellent properties inherent to PPA are compromised, and so [a ratio outside of this range] is undesirable.

Because the present invention has the above-described constitution, the polyparabanic acid compositions of the present invention have a high level of fire retardance without any loss whatsoever in the mechanical properties, electrical properties, chemical properties and appearance inherent to PPA. Hence, moldings, films, fibers and the like obtained by forming methods such as compression molding, cast film-forming techniques and melt spinning exhibit excellent performances.

The present invention is described more fully below in the examples that follow, although the invention is in no way restricted by these so long as it remains within the scope thereof. All references to parts in the examples mean "parts by weight."

The following measurement and test methods are used in the examples.

- | | |
|--|---------------------|
| • Tensile Strength, Tensile Elongation | ASTM D-882 |
| • Limiting Oxygen Index (LOI) | JIS K-7201 |
| • Self-Extinguishability | (UL standard) UL-94 |
| • Volume Resistivity | ASTM D-257 |
| • Insulation Breakdown Voltage | ASTM D-149 |
| • Dielectric Constant, Dielectric Dissipation Factor | ASTM D-150 |
| • Heat Resistance | Own company method |

(PPA specimens are suspended in a Geer oven set at 200°C, removed at fixed intervals, and subjected to a bending test. The oven life that passes this bending test is used as the measure of heat resistance.)

- | | |
|--------------------------|------------------------|
| • Peel Strength | JIS C-6481 (180° peel) |
| • Solder Heat Resistance | JIS C-6481 |

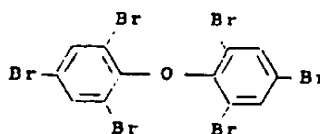
Here, the limiting oxygen index indicates a relative value for the amount of air required in cases where a fixed amount of sample continues to burn in air. The larger this numerical value, the better the self-extinguishability and the indoor fire retardance.

The following relationship exists when indicating the fire retardance by means of the limiting oxygen index and the UL standard.

<u>Limiting Oxygen Index</u>	<u>UL Standard</u>
<22.3	94HB
22.3 - 28	94V1 or 94V2
>28	94V0

Working Example 1

A PPA was synthesized in which the Ar in the general formula for PPA indicated above was a diphenylmethane-4,4'-diyl group and which had an intrinsic viscosity (η_{inh} , in DMF and at 25°C) of 1.10 was synthesized based on the disclosure in the specification of USP 3,547,897. The bromine compound represented by the formula below was added in respective amounts of 0.5 part, 1.0 part and 1.5 parts per 16 parts of a powder of this synthesized PPA, and these [combined ingredients] were dissolved in 100 parts of DMF, stirred and mixed, thereby preparing three uniform mixed solutions.



These three mixed solutions were vacuum-deaerated, after which they were cast onto glass plates and dried for 10 minutes at 150°C. The films thus obtained were peeled from the glass plates then dried for 10 minutes at 280°C, thereby giving films of three different PPA compositions, each having a thickness of 50 μ m (Experiments 1, 2 and 3). A comparative example was also carried out, in which a PPA film having a thickness of 50 μ m was obtained by exactly the same procedure, except that the above-indicated bromine compound was not added (Comparative Example 1). The mechanical strength, heat resistance of the mechanical strength, flame retardance and electrical properties of the PPA compositions films and the PPA film thus obtained are presented in Table 1. [It is apparent from this that] the PPA compositions of the present invention had an excellent fire retardance without any loss in the properties inherent to PPA.

Working Example 2

After adding 6.0 parts of the bromine compound having the formula below to 100 parts of the PPA powder obtained in Working Example 1, these were dry blended in a Henschel mixer, following which the resultant PPA composition powder was rendered into a film having a thickness of 50 μ m by using a compression molding machine set to a temperature of 350°C. The properties of the film thus obtained are presented in Table 1. This PPA composition according to

the present invention had an excellent fire retardance without any loss in the properties inherent to PPA (Experiment 4).

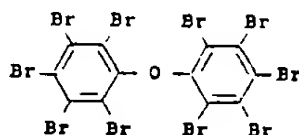


Table 1

Tests and evaluations	Units	Comparative Example 1	Working Example 1	Working Example 2	Working Example 3	Working Example 4
1) Amount of bromine compound added (parts per 100 parts of PPA)	parts	0	3.1	6.3	9.4	6.0
2) Film thickness	μ	50	50	50	50	50
3) Film color tone, transparency		good	good	good	good	good
4) Tensile strength (at break)	kg/cm^2	1200	1250	1200	1130	1210
5) Tensile elongation (at break)	%	16	15	16	15	16
6) Heat resistance at 200°C (bending test)	hours	300	350	330	310	350
7) Limiting oxygen index (LOI)	%	21.5	29.5	31.5	33.0	30.0
8) Self-extinguishability (UL-94)	Classification	94 HB	94V - 0	94V - 0	94V - 0	94V - 0
9) Volume resistivity	$\Omega - \text{cm}$	3.9×10^{16}	3.7×10^{16}	3.3×10^{16}	3.3×10^{16}	3.7×10^{16}
10) Insulation breakdown voltage	V / mil	4000	3950	4100	4000	4100
11) Dielectric constant (50 Hz)		4.0	4.0	4.1	4.0	4.1
12) Dielectric dissipation factor		0.003	0.003	0.003	0.003	0.003

Working Example 3

A PPA in which the Ar in the general formula for PPA indicated above was a diphenylether-4,4'-diyl group and which had an intrinsic viscosity (η_{inh} , in DMF and at 25°C) of 0.95 was synthesized based on the disclosure in the specification of USP 3,547,897. The bromine compound used in Working Example 1 was added in respective amounts of 0.5 part, 1.0 part and 1.5 parts per 16 parts of a powder of this synthesized PPA, and these [combined ingredients] were dissolved in 100 parts of NMP, stirred and mixed, thereby preparing three uniform mixed solutions. These mixed solutions were prepared as films of the three PPA compositions, each having a thickness of 50 μm , by exactly the same method as in Working Example 1 (Experiments 5, 6 and 7). A comparative example was also carried out, in which a PPA film having a thickness of 50 μm was obtained by exactly the same procedure, except that the above-indicated bromine compound was not added (Comparative Example 2). The various properties of these PPA compositions films and the PPA film are presented in Table 2. [It is apparent from this that] the PPA compositions of the present invention had an excellent fire retardance without any loss in the properties inherent to PPA.

Application Example 4

After adding 6 parts of the bromine compound having the formula below to 100 parts of the PPA powder obtained in Working Example 3, these were dry blended in a Henschel mixer, following which [the resultant PPA composition powder] was rendered into a film having a thickness of 50 μ m by using a compression molding machine set to a temperature of 350°C. The properties of the film thus obtained are presented in Table 2. This PPA composition according to the present invention had an excellent fire retardance (Experiment 8).

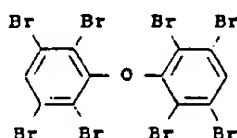


Table 2

Tests and evaluations	Units	Comparative Example 2	Working Example 5	Working Example 6	Working Example 7	Working Example 8
1) Amount of bromine compound added (parts per 100 parts of PPA)	parts	0	3.1	6.3	9.4	6.0
2) Film thickness	μ	50	50	50	50	50
3) Film color tone, transparency		good	good	good	good	good
4) Tensile strength (at break)	kg/cm ²	1300	1300	1280	1280	1290
5) Tensile elongation (at break)	%	20	20	19	18	19
6) Heat resistance at 200°C (bending test)	hours	350	360	340	330	350
7) Limiting oxygen index (LOI)	%	21.0	30.0	31.5	33.5	32.0
8) Self-extinguishability (UL-94)	Classification	94 HB	94V - 0	94V - 0	94V - 0	94V - 0
9) Volume resistivity	Ω - cm	5×10^{16}	4.9×10^{16}	5.0×10^{16}	4.7×10^{16}	4.9×10^{16}
10) Insulation breakdown voltage	V / mil	3800	3800	3800	3800	3800
11) Dielectric constant (50 Hz)		3.7	3.9	3.8	3.7	3.9
12) Dielectric dissipation factor		0.003	0.003	0.003	0.003	0.003

Working Example 5

This serves as an example of a method for preparing PPA compositions at the stage of PPA synthesis, based on the disclosure made in USP 3,547,897. In other words, a solution obtained by dissolving 53 g of hydrogen cyanide in 184 ml of NMP and a solution obtained by dissolving 490 g of 4,4'-diphenylmethane diisocyanate in 1000 ml of NMP were added dropwise at the same time to 6000 ml of an NMP solution containing 25 ml of a saturated sodium cyanide solution, and the polymerization reaction was thereby carried out. After completing dropwise addition of the hydrogen cyanide solution and the 4,4'-diphenylmethane diisocyanate solution in about 7 minutes, stirring was continued for 30 minutes. Twenty grams of triethylamine was then

added to this polymerization reaction mixture and stirring was continued for another 30 minutes. Next, 32.3 g of the bromine compound used in Working Example 1 was added and mixed into the polymerization reaction mixture thus obtained, thereby giving a uniform solution. This uniform solution was poured into a large amount of methanol and a powder-like product was precipitated out while thoroughly stirring, after which this was washed with methanol and dried, thereby giving 570 g of a PPA composition powder (intrinsic viscosity (η_{inh} , in DMF and at 25°C), 1.10) according to the present invention. Seventeen parts of a powder of this PPA composition was dissolved in 100 parts of DMF and stirred and mixed, thereby preparing a PPA composition solution. Using this solution, a 50- μ m film was obtained by exactly the same casting method as in Working Example 1 (Experiment 9). In addition, a comparative example was carried out in which, aside from not adding the bromine compound used in Application Example 1, a PPA film having a thickness of 50 μ m was obtained by exactly the same method (Comparative Example 3). The properties of the films thus obtained are presented in Table 3. [It is apparent from this that] the PPA composition according to the present invention has an excellent flame retardance.

Table 3

Tests and evaluations	Units	Comparative Example 3	Working Example 9
1) Amount of bromine compound added (parts per 100 parts of PPA)	parts	0	6
2) Film thickness	μ	50	50
3) Film color tone, transparency		good	good
4) Tensile strength (at break)	kg/cm ²	1250	1290
5) Tensile elongation (at break)	%	16	17
6) Heat resistance at 200°C (bending test)	hours	310	340
7) Limiting oxygen index (LOI)	%	21.5	32.5
8) Self-extinguishability (UL-94)	Classification	94 HB	94 V - 0
9) Volume resistivity	Ω - cm	3.9×10^{16}	3.8×10^{16}
10) Insulation breakdown voltage	V / mil	4100	4000
11) Dielectric constant (50 Hz)		4.0	3.9
12) Dielectric dissipation factor		0.004	0.004

Working Example 6

A solution obtained by dissolving in NMP 1% by weight of the PPA powder obtained in Working Example 1 was coated onto copper foil (trade name, CF3T5; manufactured by Fukuda Kinzoku) having a thickness of 3.5 μ m that had been treated for printed circuit use. The film of the PPA composition obtained in Experiment 2 in Working Example 1 was placed on top, and hot-pressing was carried out for 2 minutes at 180°C and a pressure of 10 kg/cm², following

which drying was carried out for 30 minutes at 200-220°C and for 20 minutes at 270-290°C. The composite (PPA copper-clad board) thus obtained withstood more than one minute in a solder bath at 270°C, and had a peel strength of 1.7 kg/cm. The ratio of residual solvent in this film was less than 0.1% by weight, and no changes over time in the above properties were observed even when this was stored indoors for an extended period of time. Hence, as is apparent from the above, films of the PPA compositions obtained by means of the present invention are fully capable of being used in flexible printed circuit boards.

Working Example 7

A solution obtained by dissolving 1% by weight of the PPA powder obtained in Working Example 3 in NMP was coated onto copper foil (trade name, CF3T5; manufactured by Fukuda Kinzoku) having a thickness of 35 μm that had been treated for use in printed circuits. The film of the PPA composition obtained in Experiment 6 of Working Example 3 was placed on top, and hot-pressing was carried out for 2 minutes at 180°C and a pressure of 10 kg/cm^2 , following which drying was carried out for 30 minutes at 200-220°C, and for 20 minutes at 270-290°C. The composite thus obtained as a result (PPA copper-clad plate) withstood a 270°C solder bath for more than one minute, and the peel strength was 1.7 kg/cm. The ratio of solvent remaining in this film was no more than 0.1% by weight, and no changes over time in the above properties were observed even during long-term indoor storage. Hence, as is apparent from the above, films of the PPA compositions obtained by means of the present invention are fully capable of being used in flexible printed circuit boards.

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